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Quantum-chemical calculations of dye-sensitized semiconductor nanocrystals

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ABSTRACT

Quantum chemical calculations providing detailed information of dye-sensitized semiconductor nanocrystals are presented. The calculations are used to elucidate both structural and electronic properties of photoelectrochemical devices, such as environmentally friendly Dye-Sensitized Solar Cells (DSSCs), at the molecular level. Quantum chemical calculations have recently been performed on both organic and organometallic dye molecules attached to titanium dioxide (TiO₂) nanocrystals via different anchor and spacer groups. Strategies to make accurate quantum chemical calculations, e.g. at the DFT level of theory, on increasingly realistic models of such dye-sensitized semiconductor interfaces are presented. The ability of different anchor and spacer groups to act as mediators of ultrafast photo-induced electron injection from the dye molecules into the semiconductor nanocrystals is, in particular, discussed in terms of calculated electronic coupling strengths, and direct comparisons with experimental information are made whenever possible. Progress in the development of multi-scale simulation techniques using so called reactive force fields is illustrated for dye-sensitized solar cell systems.

Keywords: Quantum Photoelectrochemistry, Dye-sensitized solar cells, TiO₂, nanocrystals, Surface Electron Transfer, Multi-scale simulations

1. INTRODUCTION

Quantum chemical calculations can provide detailed information about the structural and electronic properties of dye-semiconductor interfaces.¹ Such calculations therefore offer a way to predict many physical and chemical properties of these interfaces from first principles, i.e. without having to introduce empirical or adjustable parameters. As such, the calculations can complement experimental efforts to both characterize fundamental optoelectronic properties of dye-semiconductor interfaces², and to develop photoelectrochemical devices based on such heterostructures.³

One of the most intriguing properties of dye-sensitized semiconductor surfaces is the ultrafast electron transfer rates, often taking place on a sub-100 femtosecond timescale, that have been observed for photoinduced surface electron transfer across many molecule-semiconductor interfaces following photo-excitation of both organic and organometallic dyes.⁴ In terms of emerging technology, these interfaces form an essential ingredient in so called dye-sensitized solar cells (DSSCs), which potentially offer an inexpensive and environmentally-friendly alternative to traditional photovoltaic devices.³

The possibilities to perform accurate calculations have, however, so far been seriously limited by the structural complexity of typical dye-sensitized metal oxide nanocrystalline materials. Realistic atomistic simulations typically require hundreds or thousands of atoms to be included in the model, and this makes calculations extremely demanding in terms of memory and CPU usage. In this relatively new field of application of advanced atomistic simulations, it is important to establish atomistic model systems which simultaneously are sufficiently realistic to give accurate predictions and at the same time are manageable computationally.

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It is also important to develop new computational methods that can bridge the gap in length- and time-scales from what can normally be treated using quantum mechanical modelling, i.e. stationary properties or femtosecond processes in few-nanometer sized systems, to what happens in reality which can often involve picosecond or longer processes in systems of nanometer to micrometer size.

Here, a brief overview of some of our recent work devoted to performing more and more realistic atomistic calculations of dye-sensitized nanocrystalline TiO_2 systems is presented. This includes detailed analysis of electronic structure calculations for both ruthenium polypyridyl and perylene dyes in order to estimate surface electron transfer rates from the interfacial electronic coupling. In particular, the role of anchor and spacer groups as mediators of surface electron transfer processes is discussed. Finally, some results pertaining to the development of a multi-scale simulation technique involving so called reactive force fields, designed to allow molecular dynamics simulations of chemical reactions at complex metal oxide surfaces are presented.

2. METHODS

2.1 Quantum chemical calculations

It is possible to study nanocrystalline materials using either cluster or periodic calculations. We have in particular investigated a set of cluster models representing anatase TiO_2 nanocrystals with diameters exceeding 1nm. These model nanocrystals can be used to investigate dye-sensitized nanocrystals using standard quantum chemical methods, e.g. at the density functional theory (DFT) and the time-dependent DFT (TD-DFT) levels of theory.⁵ A combination of hybrid functionals, especially B3LYP, and basis sets of valence double-zeta or better quality together with effective core potentials (ECPs) replacing the inner-shell electrons has been found to work well for reasonably fast and accurate calculations, including both geometry optimizations and electronic structure analysis.¹

2.2 Newns-Anderson model of interfacial electronic coupling

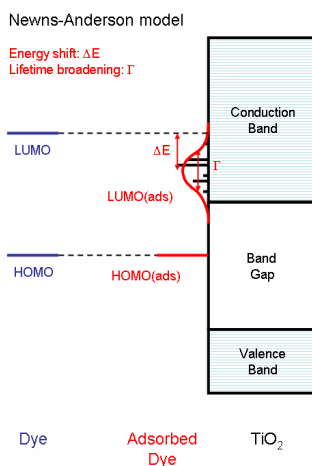


Fig. 1 Newns-Anderson model of resonant electronic coupling of a photo-excited dye with the TiO_2 conduction band.

Ultrafast photoinduced surface electron transfer across the dye- TiO_2 interface on a sub-100 fs timescale can be rationalized in terms of resonant coupling of the excited state of the dye with the conduction band of the substrate in cases when the excited state is located sufficiently high above the conduction band edge in order to realize the so called wide band limit.⁶ According to a Newns-Anderson type model of resonant electronic coupling across the interface, this effect expresses itself as a lifetime broadening of the relevant excited electronic level, e.g. corresponding to the lowest unoccupied molecular orbital of the adsorbate (LUMO(ads)). The broadening is in general also accompanied by a shift

of the adsorbed level compared to its desorbed energy. This is shown schematically in Fig. 1. Both the energy shift and lifetime broadening can be estimated from a careful analysis of the electronic structure calculation of the combined dye-semiconductor system, according to a recently tested procedure involving a fitting of the LUMO(ads) contributions to a Lorentzian function.

2.3 Reactive force fields for multi-scale simulations

Some results are here presented for the development of a multi-scale computational strategy for atomistic simulations of dye-sensitized solar cells combining DFT calculations with the new ReaxFF reactive force field in molecular dynamics (MD) simulations to predict the structures of these complex metal oxide interfaces under both equilibrium conditions and dynamically. The first-principles based ReaxFF reactive force fields have been shown to reproduce energy surfaces, structures, and reaction barriers from accurate quantum-chemical calculations for a wide range of materials including e.g. hydrocarbons⁷, metal oxides⁸, and mixed organic-metal oxide systems.⁹

In general terms, the ReaxFF method includes a set of features which goes beyond most classical force field methods, and makes it a versatile tool for studying chemical structures and reactions in complex systems. In particular, the inclusion of environment-dependent atomic charges, bond-order dependent valence terms, and non-bonded interactions allows for simulations of chemical reactions with no discontinuities in energies or forces, transferable potentials, and no need to predefine reactive sites. It can therefore be said to bridge the gap between quantum mechanical (QM) and classical force field molecular dynamics (MD) simulation techniques in terms of system time- and length-scale applicability. This is illustrated in Fig. 2. It is parameterized against periodic and non-periodic quantum mechanical calculations, including both solid and gas phase structures and reactions. Picosecond or longer MD simulations can be performed e.g. as NVT simulations of systems containing thousands of atoms at moderate computational cost. We are currently extending this method for studies of dye-sensitized solar cells by development of parameters for titanium oxides and their interactions with different adsorbates, including all necessary parameters for typical dye-sensitized interfaces.

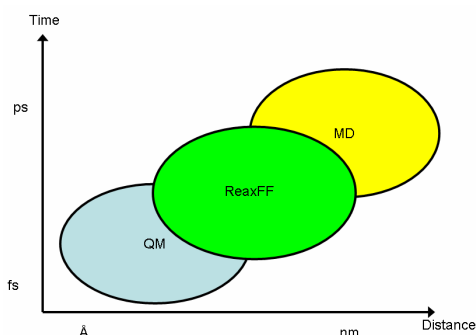


Fig 2 Using the reactive force field method ReaxFF to bridge the time- and length-scale gap between quantum mechanical (QM) and molecular dynamics (MD) methods. The ReaxFF method allows picosecond molecular dynamics simulations of systems containing thousands of atoms while retaining the capability of modelling bond breaking and bond making processes normally only possible to achieve with time-consuming QM methods.

3. RESULTS

3.1 Dye-sensitized solar cells: N3 - TiO₂

A prime target for theoretical modelling of DSSCs and related systems is to perform accurate calculations of the most common and efficient supramolecular systems including ruthenium polypyridyl dyes bound to nanocrystalline TiO₂ electrodes. The so called N3 dye has, in particular, for a long time served as a standard dye against which the performance of new dyes is compared. Recently, we performed calculations of structural and electronic interactions

between this N3 dye and a small TiO_2 nanoparticle with a diameter of ca 1.2 nm.¹⁰ The calculations illustrate that there is sufficient structural flexibility in the system for the formation of a structurally stable interface between the dye and the substrate with two or more anchor groups from the dye binding to the substrate simultaneously. Although the TiO_2 model nanocrystal is so small that it has a somewhat too large band gap due to quantum size effects, the general features of the calculated electronic structure agree well with what is known experimentally about this system. The calculated (DFT) electronic structure is shown schematically in Fig. 3. There is a well developed substrate band structure comprising a fully occupied valence band, a large band gap of ca 4 eV, and a completely empty conduction band. The dye contributes occupied mixed Ru(4d)-NCS(π) levels in the band gap which are very similar to those which have been found for the isolated dye. The first unoccupied adsorbate molecular orbital is found close to the conduction band edge. Although it is difficult to compare the interfacial level alignment directly with experiments where e.g. larger TiO_2 nanoparticles have been used, the location of the calculated LUMO(ads) level close to the conduction band edge is compatible with the biphasic injection that has been observed experimentally and which suggests that the lowest relaxed triplet states of the dye lie below the conduction band edge.¹¹

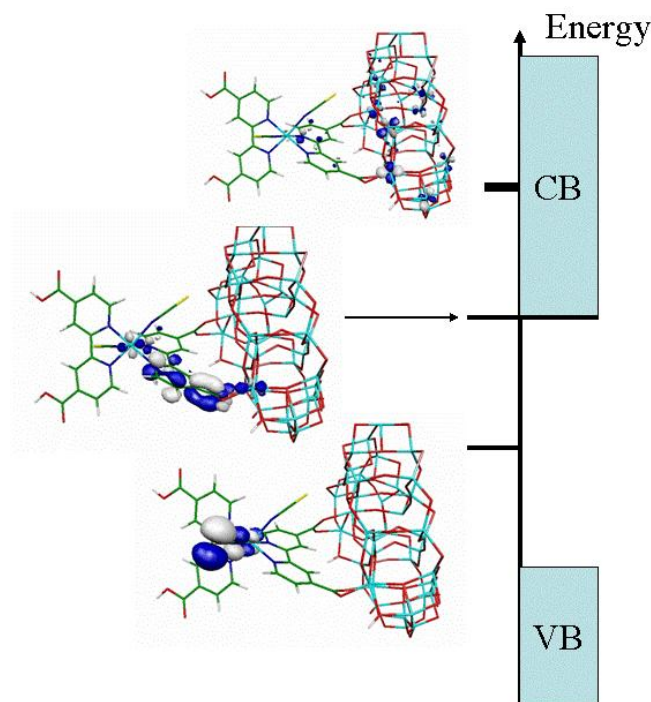


Fig. 3 Energy level diagram for N3 adsorbed on a $(\text{TiO}_2)_{38}$ nanoparticle with a diameter of 1.2 nm.

3.2 Surface electron transfer through spacer groups: Perylene - TiO_2

It is interesting to consider the possibilities to influence the surface electron transfer rates both in the forward and backward direction through chemical control of the interface. One way to achieve such control is to modify the anchor group that links the dye to the semiconductor, either by replacing it or by the insertion of spacer groups between the anchor group and the dye. This is illustrated schematically in Fig. 4. It is in this context important to understand if the anchor or anchor-cum-spacer group acts as a mediator of surface electron transfer reactions, or if there is an effective tunnelling barrier due to the presence of the anchor or anchor-cum-spacer which slows down surface electron transfer reactions.

A set of three substituted perylene molecules attached to TiO_2 was recently investigated theoretically, see Fig. 5.⁶ All three sensitizers bind to the TiO_2 via a single carboxylate anchor group. In the first case, this anchor group is directly attached to the perylene unit. In the second cases a saturated ($-\text{CH}_2-\text{CH}_2-$) spacer group is inserted between the

perylene and the carboxylate anchor group. In the third case, an unsaturated ($-\text{CH}=\text{CH}-$) spacer group is inserted between the perylene and the carboxylate. First the electronic structures of the free molecules were considered, and a clear difference is found for the molecule with the saturated spacer group in the sense that the saturated spacer group clearly prevents the delocalization of the LUMO π^* orbital onto the anchor-cum-spacer group.

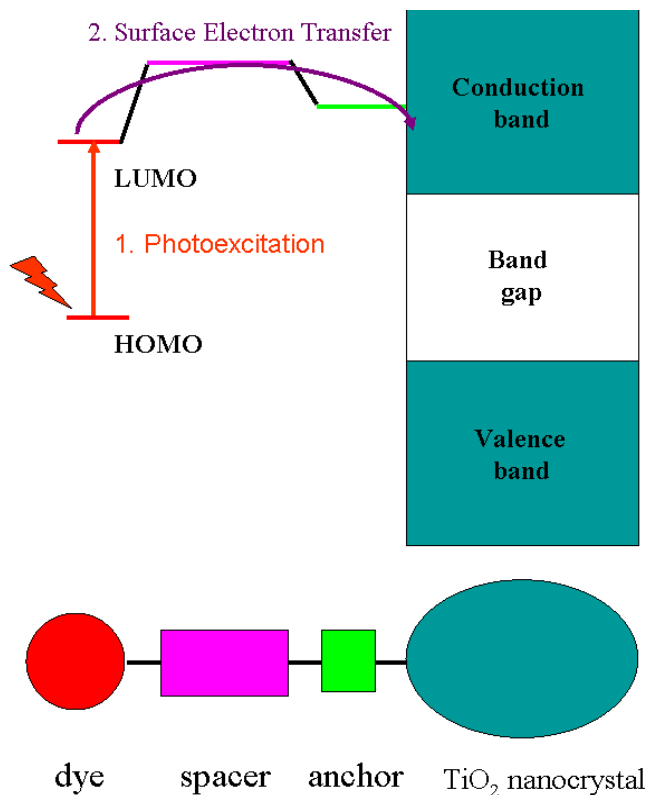


Fig. 4 Schematic illustration of photoinduced surface electron transfer through anchor and spacer groups.

Each of the three molecules was subsequently attached to a 2 nm model TiO_2 nanocrystal, and the electronic structures of the combined systems were computed at the DFT level of theory. Using the Newns-Anderson type approach outlined in the methods section, surface electron transfer times could be estimated from the calculated energy broadenings of the respective LUMO(ads) levels. The calculated surface electron transfer times are listed in Fig. 5 together with pictures of the free LUMO levels and pictures of the model interfaces. In all cases the calculated injection times are sub-100 fs. The system with the saturated spacer is, however, calculated to have a significantly weaker electronic coupling compared to the other two systems. Encouragingly, these findings are consistent with experimental evidence for directly comparable systems both in terms of the order of magnitudes of the injection times and in terms of the relative trends for the series of systems.⁶

The results indicate that, at a qualitative level, the lack of delocalization of the LUMO(ads) level on the saturated anchor-cum-spacer group in the $\text{Pe-CH}_2\text{-CH}_2\text{-COOH}$ system, decreases the electronic coupling significantly. For the Pe-COOH and $\text{Pe-CH}=\text{CH-COOH}$ systems, on the other hand, the anchor-cum-spacer groups instead facilitate long-range electron transfer by providing an effective electronic bridge between the dye and the substrate. It is also interesting to note that the electron transfer rate is significantly different for the two systems with spacers, although the perylene- TiO_2 distance is very similar. This clearly suggests that the distance dependence of electron transfer is highly dependent on the chemical nature of the spacer group. It will be interesting to extend this investigation to a broader range of systems in order to try to arrive at more general and quantitative conclusions in this respect.

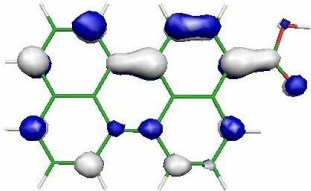
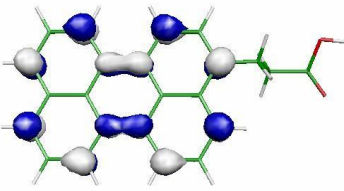
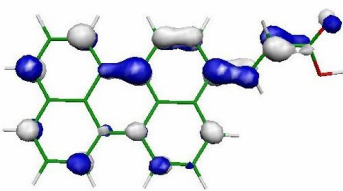
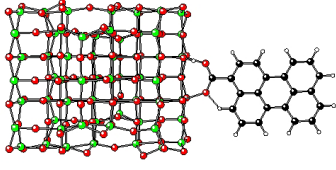
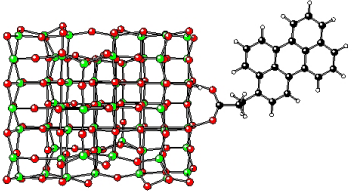
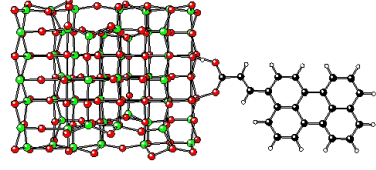
Pe-COOH	Pe-CH ₂ -CH ₂ -COOH	Pe-CH=CH-COOH
		
		
$\tau_{\text{calc}} = 5 \text{ fs}$	$\tau_{\text{calc}} = 33 \text{ fs}$	$\tau_{\text{calc}} = 10 \text{ fs}$

Fig. 5 Illustration of the dependence of photoinduced surface electron transfer times from a dye molecule to a semiconductor on the delocalization of the lowest unoccupied molecular orbital (LUMO) across the anchor and spacer groups. In the wide-band limit, a large degree of delocalization favours a strong electronic coupling of the excited state of the chromophore with the substrate bands.

3.3 Environmental effects: Ru-dyes with OPE rigid rod linkers in different chemical environments

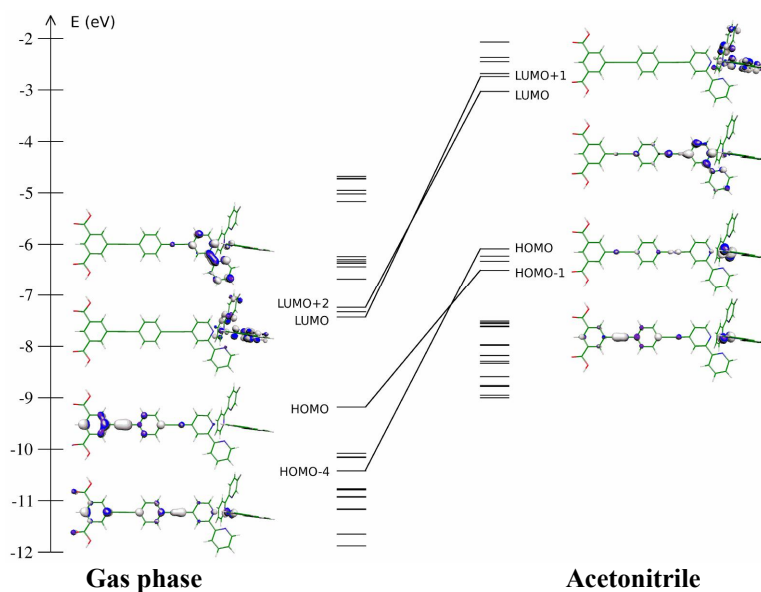


Fig. 6 Calculated effect of chemical environment on the frontier molecular orbital ordering. B3LYP/LANL2DZ results are shown for vacuum (left) and acetonitrile (right) environments. The large differences of the frontier molecular orbital ordering is ascribed to the difference in screening of the positive charge on the metal ion in the different environments.

The chemical environment can have a significant influence on the optoelectronic properties of dye-sensitized semiconductor interfaces, and this needs to be taken into account in order to make accurate theoretical predictions. We have recently compared results from calculations of a series of ruthenium tris-bipyridine dyes carrying so-called rigid rods in different chemical environments.¹² This is illustrated in Fig. 6 for $[\text{Ru}(\text{bpy})_2\text{bpy-E-Ph-E-Ipa}]^{+2}$ (bpy = 2,2'-bipyridine, E = ethynylene, Ph = *p*-phenylene, Ipa = isophthalic acid) in gas phase and in a polarisable continuum model (PCM) treatment of acetonitrile. There is a substantial rearrangement of the frontier molecular orbital ordering between the different environments. This also influences many properties, including significant differences in the calculated absorption spectra and redox properties relevant for the use of the rigid rods as mediators of photoinduced surface electron transfer.

In this case, the strong rearrangement of the electronic structure is evidently related to the screening of the positive charge on the ruthenium ion. The presence of unscreened metal ions is perhaps somewhat unrealistic under ordinary experimental conditions, and this can to some extent therefore be classified as primarily a computational concern. Nevertheless, it illustrates that the environment does play an important role for many optoelectronic properties, and that e.g. the energy alignment of frontier orbitals depends on the particular experimental conditions. Some differences can, for example, be expected in similar systems depending on the dielectric constant of the solvent, and the presence of counter ions. Considerations along these lines also open up interesting possibilities to tune the electrochemical or optoelectronic properties by altering the chemical environment.

3.4 Multi-scale simulations of dye-sensitized solar cells

The development of a first-principles based multi-scale simulation technique centred around the use of ReaxFF reactive force fields for advanced MD simulations requires a large number of force field parameters to be determined from quantum mechanical (QM) data. When an initial set of parameters has been determined based on an extensive training set containing data from both molecular and periodic calculations, it becomes possible to start simulation tests. The simulations generate new structures and reaction pathways, the accuracy of which can be verified using QM methods. This makes the generation of the reactive force field parameters an iterative procedure in which the parameter set is gradually improved to more and more accurately describe the chemical interaction of interest. An illustration of a test simulation of formic acid adsorption on the rutile (110) surface of TiO_2 is shown in Fig. 7.

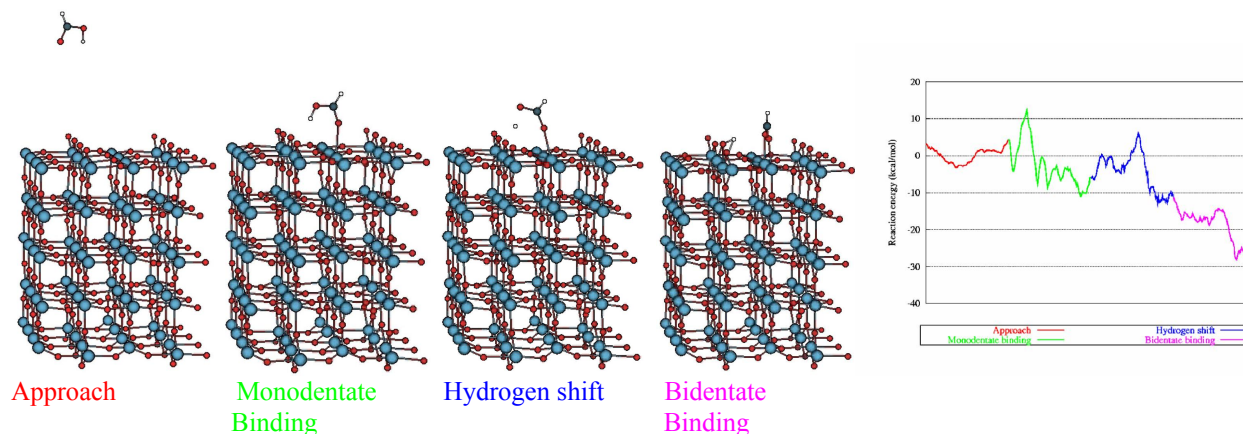


Fig. 7 Low temperature molecular dynamics simulation of reaction profile for formic acid adsorption on TiO_2 rutile (110). Left four panels show snapshots of the different reaction steps. Right panel shows the corresponding energy profile. Note in particular the continuous description of the bond breaking and bond making processes taking place both in the molecule and between the molecule and the surface.

A set of reactive force field parameters is being developed for titanium oxide systems interacting with organic and organometallic adsorbates. These parameters are currently being tested for MD simulations of dye-sensitized TiO_2 systems. As an example, Fig. 8 shows a snapshot from a high-temperature simulation testing the stability of the interface formed when ruthenium dye molecules are bound to TiO_2 nanocrystalline materials.

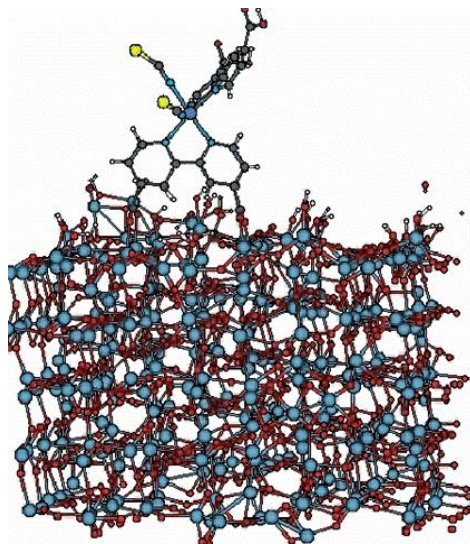


Fig. 8 Snapshot from a high temperature MD simulation (10 ps, 1000 K) of the stability of an interface composed of the N3 ruthenium dye adsorbed on a TiO_2 surface.

4. CONCLUSIONS

A better understanding of some of the basic structural and optoelectronic properties of dye-sensitized TiO_2 nanocrystalline materials is gradually emerging from a combination of experimental evidence and first-principles based atomistic modelling. In terms of the calculations, it has recently become possible to perform first principles atomistic modelling of dye-sensitized TiO_2 nanocrystalline materials that are sufficiently realistic to allow comparisons with experiments performed on directly comparable systems. This provides significantly enhanced possibilities to understand the basic structural and optoelectronic interfacial interactions in detail. For example, it is now possible to consider the structural stability of different atomistic models of technologically important interfaces between e.g. ruthenium dyes and TiO_2 nanocrystalline materials, as well as to study the interfacial electronic interactions.

By considering the evidence from the calculations of several organic and organometallic dyes anchored to TiO_2 surfaces and nanocrystals, it appears that the intriguing sub-100 fs ultrafast photoinduced electron injection times that have been reported from experiments on several interfacial systems can largely be explained by the active role of common anchor groups, such as carboxylic acids, to mediate resonant electronic coupling between the excited state of the dye and the TiO_2 conduction band. This is frequently evidenced already in the molecular orbital structure of the free dye, and injection times appear to be successfully estimated in the wide band limit using a relatively simple Newns-Anderson electronic coupling model applied to the electronic structure calculated for the combined dye-semiconductor system. However, some evidence suggests that the energies of the anchor group frontier orbitals can be significantly influenced by the binding to the metal oxide substrate. This dependence is difficult to predict from purely molecular calculations, and accurate predictions of the interfacial electronic interactions are therefore likely to require the use of relatively time-consuming calculations of combined dye-semiconductor systems.

The development of multi-scale simulation techniques for the surface chemistry of titanium oxides opens up significantly enhanced possibilities to study more complex systems in longer simulations. This is likely to accelerate the progress in the modelling capabilities in the near future, with possibilities to investigate more complex systems, e.g.

allowing systematic studies of the role of defects and doping, as well as the chemical environment. The emerging possibilities to combine quantum-chemical calculations and advanced molecular dynamics simulations in a multi-scale approach significantly improves the prospects of rationally designing better photoelectrochemical devices based on dye-sensitized metal oxide materials.

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